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Journal of Alloys and Compounds 323–324 (2001) 190–192

Journal of ALLOYS AND COMPOUNDS

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Europium(III)–asparagine complexation in aqueous methanol

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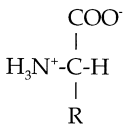
Abstract

A problem of long-term interest in lanthanide chemistry is whether a ligand resides in the cation's inner or outer solvation shell. Using asparagine as part of a study of Eu(III) and amino acids to determine complexation differences, only the one-to-one complex forms and the complexation thermodynamics are consistent with inner-sphere complexation. The substitution of water by methanol causes only a small increase in the complexation constant.

Keywords: Europium complexes; Asparagine; Inner-sphere complexes; Outer-sphere complexes

1. Introduction

As part of a long-term investigation of the complexation between lanthanides and molecules of biochemical interest, we have initiated this study of the complexation between europium(III) and the amino acid asparagine. Our interest in the chemistry of lanthanide–amino acid complexes is to determine if: (1) outer- or inner-sphere complexes are present in water; (2) the addition of a less hydrophilic solvent, such as methanol, would change the distribution of complexes; (3) changing the solvent causes a lanthanide coordination number change; and (4) there is a correlation between ligand structure and the complexation constants and thermodynamics. Information about the change in the number of water molecules in the inner solvation shell due to complexation can be determined by Horrocks' luminescence lifetimes method [1]. We have been investigating the complexation between Eu(III) and amino acids in aqueous methanol in an attempt to understand the binding of Eu(III) to these molecules of biochemical interest [2–4]. Choppin [5] has utilized complexation thermodynamics to differentiate between inner- and outer-sphere complexation. Under this model, inner-sphere complexes have positive enthalpies and entropies, and outer-sphere complexes have negative enthalpies and entropies [5]. Both thermodynamic and ultrasonic relaxation measurements had demonstrated that inner-sphere complexes form between Eu(III) and glycine in water [2]. Glutamine and serine complexes with Eu(III) in water also had positive complexation enthalpy and entropy and, thus, the complexes were predicted to be inner sphere [4]. A different result occurs with alanine, where the enthalpy and entropy are both negative, indicating that outer-sphere complexes may be present [3]. The amino acids, of general formula:



were all investigated in the pH range where the zwitterion is the predominant species. This investigation with asparagine was initiated as the final part of our studies to determine if changes in the R-group effect the complexation.

2. Experimental

The experimental procedures are similar to those used with the other amino acids we have studied [4]. After dissolving dried Eu_2O_3 (Molycorp) in a slight excess of $HClO_4$, the stock solutions were standardized by EDTA titrations. L-Asparagine (99%, Sigma) was used without further purification. At constant europium and asparagine concentrations, the absorbance is independent of pH from pH 2 to pH 6, indicating that a proton is not released upon complexation and, thus, that complexation does not affect the ionic strength, which was kept at 1.0 M in perchlorate media by using 0.167 M $Eu(ClO_4)_3$ with small quantities of $HClO_4$ or NaOH to adjust the pH. No attempt was made to correlate the pH-meter reading with real solution acidities in aqueous methanol since we work in a region

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PII: S0925-8388(01)01132-X

where the complexation is pH-independent and the meter is used to ensure that we stay in this region. Thermostated Cary 3 spectrometers were used to record the absorbance for each solution at 15, 20, 25 and 37°C. The addition of perchlorate at constant europium concentrations does not change the absorbance, whereas the addition of asparagine increases the absorbance, and was attributed to complexation between Eu(III) and the amino acid with a higher extinction coefficient for the complex than for the free Eu(III) ion. Measurements were carried out from 250 to 500 nm, with absorption at 464.8 nm being used to determine the complexation constants. As before, the Benesi-Hildebrand method is used to evaluate the complexation constants [5,6]. Difference spectra between the test solution containing the Eu(III), the amino acid and the solvent versus the reference solution containing the metal ion, ionic media, and the same solvent as the test solution were obtained using matched 1.00-cm cells (Helma).

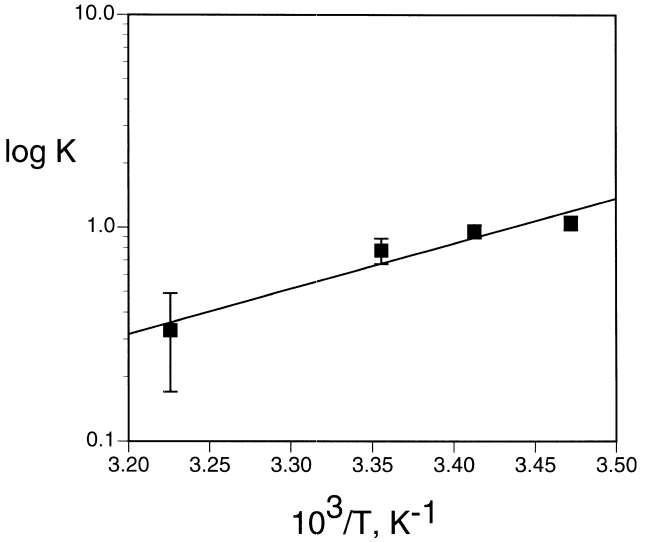

Fig. 1. Variation of the equilibrium constant with temperature in 40% water.

3. Results and discussion

The Benesi-Hildebrand method resulted in a linear relationship at each solvent and temperature studied, attributed to the formation of only the one-to-one complex between Eu(III) and the asparagine. Although the Benesi-Hildebrand equation is only an approximation, recent results using Ni(II) with thiocyanate have shown that, under the conditions where it is not valid, systematic deviations from linearity are observed [7]. Each of the Benesi-Hildebrand plots involves more than 50 experimental solutions. However, since the complexation constants are relatively small, the error in each equilibrium constant is typically within 10 to 20%. At each solvent composition, the variation between the log *K* and the reciprocal of the absolute temperature, known as the van't Hoff plot, gives the complexation enthalpy from the slope and the entropy from the intercept. Fig. 1, in 40% water–60% methanol, is a typical plot. Figs. 2–4 summarize the asparagine data in comparison to that of the other four amino acids studied under the same conditions of metal-ion concentration, solvent composition, temperature and pH [2–4]. Only the simplest amino acid, glycine, where the R-group is a hydrogen atom, has a large increase in its complexation constant as methanol replaces water as the solvent. The variation of the equilibrium constants for each amino acid does not vary in a similar manner for each of the acids, and no systematic variation is detected. The asparagine result is more similar to the other three amino acids. When we initiated this series of studies, we had hoped that either steric effects or different types of moieties would change the equilibrium constants in a way that can correlate with amino-acid properties. Unfortunately, this has not been the case. We can conclude that the bonding is between the lanthanide cation and the negatively charged oxygen of the carbonic acid group. The observation that the complexation constants are several orders of magnitude less than the corresponding acetate system [8] is consistent with our hypothesis that the complexation between europium(III) and the simple amino acids is with the zwitterion form of the amino acid. The protonated amino group near the carboxyl ion successfully repels the lanthanide ion and significantly lowers the complexation.

Figs. 3 and 4 represent the enthalpy and entropy of complexation as a function of solvent. Asparagine has positive enthalpy and entropy of complexation in water, which is consistent with the hypothesis that inner-sphere complexes are formed. Only the alanine system in water is clearly not inner sphere, based upon the complexation thermodynamics. Both glutamine and asparagine have a minimum in enthalpy at around 40% water. Since the

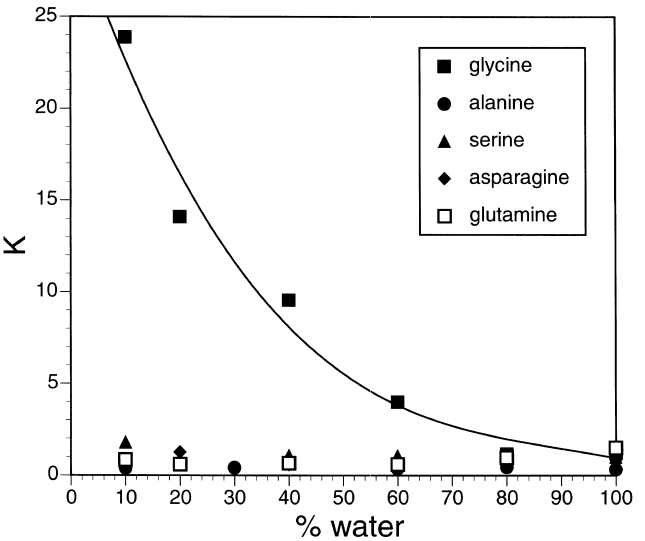

Fig. 2. Variation of the Eu(III)–amino acid equilibrium constants at 25°C with water.

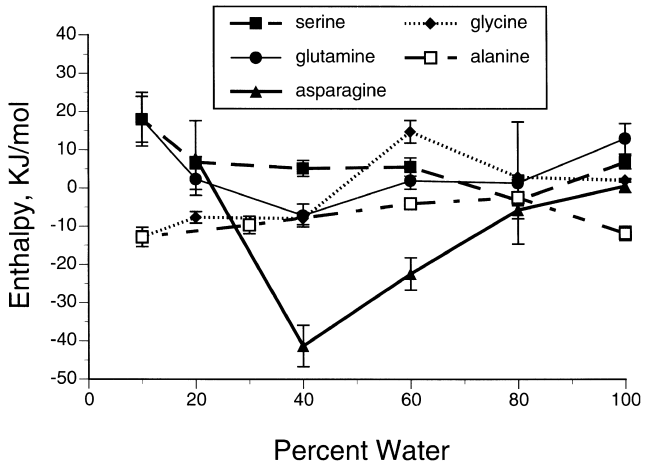

Fig. 3. Complexation enthalpies for Eu(III) with amino acids in aqueous methanol. No systematic variation with amino-acid structure is found.

R-chain is longer in glutamine than asparagine, and since the effect is greater for asparagine, the minimum does not correlate with chain length. However, we believe that this tail may affect the solvation shell around the amino acid and that this causes the enthalpy differences. It is interesting to note that glycine has a maximum in enthalpy at around 60% water. Although differences in the thermodynamics are dependent upon the amino acid, some general comments can be made. Since the equilibrium constants are near unity, the complexation enthalpy and entropy terms are very similar, with the same trends. As methanol is initially added to the solvent mixture, the equilibrium constant is relatively constant, within experimental error. However, both the complexation enthalpy and entropy decrease. Based upon our early ultrasonic experiments on lanthanide complexation, the addition of methanol increases inner-sphere complexation, but also enhances outer-sphere complexation [9]. Since outer-sphere complexes lower the enthalpy and entropy, it is not surprising that these parameters decrease. As methanol continues to increase, the relative percentages of inner-sphere complexes also increase and the complexation thermodynamic parameters become more positive. These minima in enthalpy and entropy are not uncommon in mixed solvents. The ultrasonic technique was used to interpret these maxima and minima in thermodynamic parameters with solvent composition in terms of complexation-induced coordination-number changes.

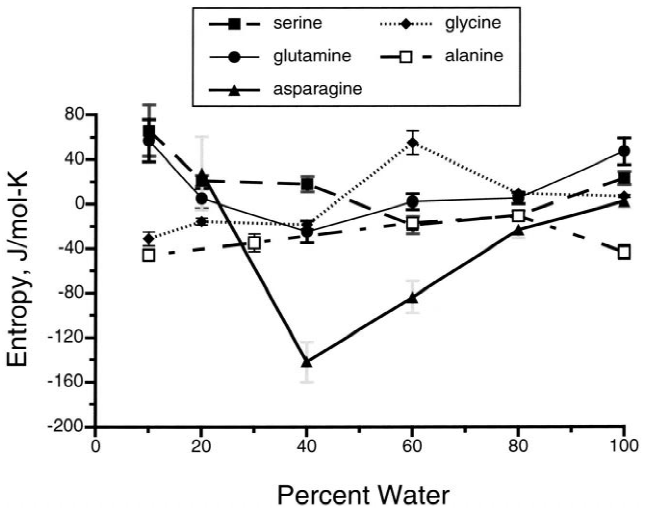

Fig. 4. Complexation entropies for Eu(III) with amino acids in aqueous methanol. No systematic variation with amino-acid structure is found.

In conclusion, the predominant species present in lanthanide–amino acid complexes is an inner-sphere complex between the cation and the zwitterion. For simple amino acids, structural differences in the amino acid appear to have little effect upon the complexation itself. The addition of a less hydrophilic solvent, such as methanol, does decrease the solvent's dielectric constant and, hence, does increase the complexation constant between europium(III) and the carboxylate group.

Acknowledgements

We would like to acknowledge the financial support of the Petroleum Research Fund administered through the American Chemical Society Grant #32100-B3 and the National Institutes of Health Minority Biomedical Research Support (MBRS) Program Grant 2 S06 GM08192 for the support for this research.

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